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Oxidation of Tricarbonyl(η^1,η^2-but-3-en-1-yl)iron(0) and Tricarbonyl(η^3-allyl)iron(0) Anion Complexes with Dioxygen

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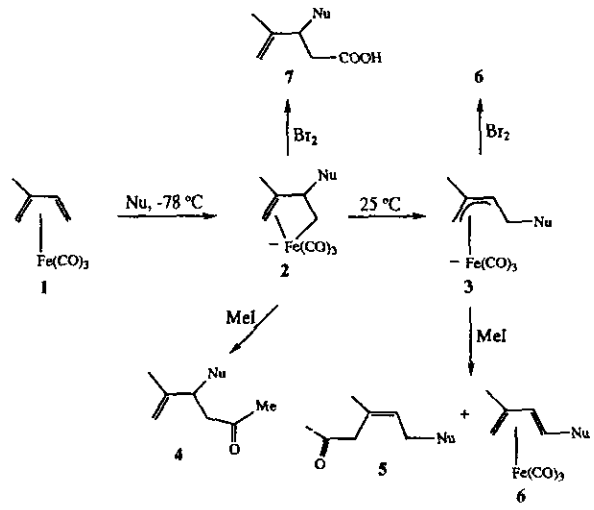
The addition of reactive carbanions to tricarbonyl(η^4-1,3-diene)iron(0) complexes proceeded at -78 °C to give putative tricarbonyl(η^1,η^2-but-3-en-1-yl)iron(0) anion complexes and at 25 °C to produce postulated tricarbonyl(η^3-allyl)iron(0) anion complexes; trapping of reactive intermediates with dioxygen produced γ,δ-unsaturated acids and allylic alcohols, respectively.

INTRODUCTION

There is increasing interest in the use of transition metals to activate unsaturated hydrocarbon ligands. Polyene ligands containing neutral or cationic metal carbonyl moieties are normally activated toward addition of nucleophiles.[1] Semmelhack and corworkers found that reactive carbanions added to (η^4-1,3-isoprene)$Fe(CO)_3$ (**1**) to produce tricarbonyl(η^1,η^2-but-3-en-1-yl)iron(0) anion **2** at -78 °C (kinetically controlled reaction) and tricarbonyl(η^3-allyl)iron(0) anion **3** at 25 °C (thermodynamically controlled reaction).[2] Brookhart showed that (η^3-allyl)$Fe(CO)_3$ anionic complexes were also generated on reduction of (η^3-allyl)$Fe(CO)_3I$ complexes with sodium-mercury amalgam or on hydride reduction of (η^4-1,3-diene)$Fe(CO)_3$ complexes.[3] Before our work, various electrophiles were used to trap these two intermediates. For instance, reaction of **2** with methyl iodide give ketone **4**,[4] whereas quenching of **3** with methyl iodide produced ketone **5** and nucleophilic substituted diene-iron complex **6**,[5] and addition of excess dibromine to **2** and **3** gave acid **7** and complex **6**, respectively, in moderate yields (Scheme I).[6] However, the reaction of reactive intermediates **2** and **3** with dioxygen has not been explored. We report here that trapping of (η^1,η^2-but-3-en-1-yl)$Fe(CO)_3$ (homoallyl) and (η^3-allyl)$Fe(CO)_3$ (allyl) anion intermediates with molecules of oxygen generates γ,δ-unsaturated acids and allylic alcohols, respectively.

Scheme I



RESULTS AND DISCUSSION

Reaction of (η^4-diene)$Fe(CO)_3$ complexes with a reactive carbanion (1.2 molar proportions) in THF/HMPA at -78 °C for 2 h followed by oxidation of the reaction mixture with dioxygen gave γ,δ-unsaturated acids in good yields (61-84%) (Table 1) after acid is quenching. The results are consistent with oxidation of homoallyl anion intermediate **2** with dibromine.[6a] A mechanism is proposed to form carboxylic acid derivatives (**12-15**, Table 1), which is illustrated in Scheme II. Initial addition of the nucleophile at the internal position of complex **1** at -78 °C would give homoallyl intermediate **16**. Oxidation of **16** followed by acid is quenching led to formation of acid **12**. This reaction pathway is also proposed for alkylation and bromination of the tetracarbonyliron dianion (known as the Collman reagent).[7] Several entries in Table 1 deserve special mention. The addition followed by trapping of starting complex **10** with a methoxy group at C-2 of the diene ligand gave bicyclic lactone **15** in 65% yield (entry 4, Table 1). The formation of **15** presumably derived from intramolecular cyclization of zwitterion

Scheme II

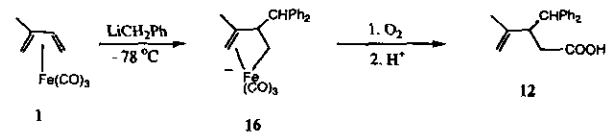
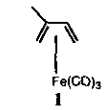
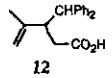
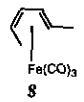
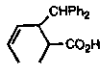
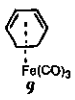
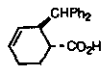
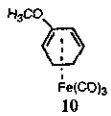
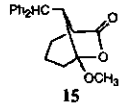


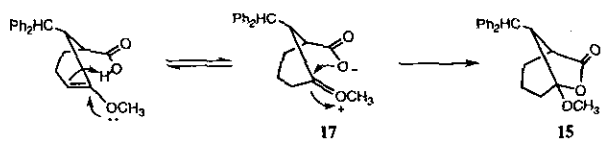
Table 1. Reaction of (η^1,η^2-But-3-en-1-yl)Fe(CO)$_3$ Anionic Complexes with Dioxygen

Entry	Complex	Nucleophile	Oxidant	Product[a]	Yield[b]/%
1	 1	$LiCHPh_2$	O_2/H^+	 12	61
2	 8	$LiCHPh_2$	O_2/H^+	 13	84
3	 9	$LiCHPh_2$	O_2/H^+	 14	63
4	 10	$LiCHPh_2$	O_2/H^+	 15	65
5	1	$LiCHPh_2$	O_2, PhCHO/H^+	12	56
6	1	$LiCHPh_2$	CAN/H_2O	12	46

[a] Spectral data of all compounds were consistent with those in our previous results.
[b] Yields are based on isolated yields of analytically pure compounds.

17 (Scheme III).[6a] Murahashi reported that oxidation of alkanes and alkenes with dioxygen in the presence of aldehydes performed efficiently to give alcohols.[8] Therefore, benzaldehyde was added in the expectation that the extra oxygen atom would be trapped. Addition of benzaldehyde before acid is quenching, however, did not increase the yield of the acid (entry 5, Table 1). Furthermore, oxidation of homoallyl anion intermediate **16** with CAN (ammonium cerium IV nitrate) produced acid **12** in 46% yield (entry 6, Table 1). Thus, dioxygen is the most efficient oxidant to oxidize **16** in our work.

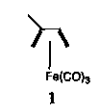
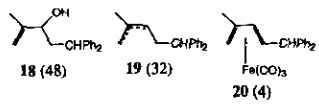
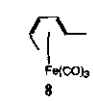
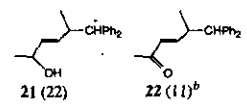
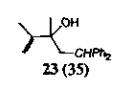
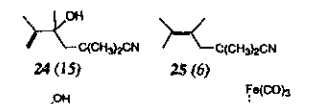
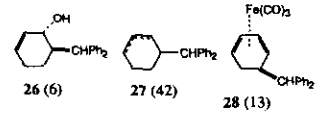
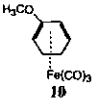
Scheme III



Treatment of (η^4-isoprene)Fe(CO)$_3$ complex (**1**) with a lithiodiphenylmethane (1.2 molar proportions, see experimental section) in THF/HMPA (3/1, 25 °C, 2h) followed by addition of dioxygen and then trifluoroacetic acid gave allylic alcohol **18** (48%), olefin **19** (32%) and complex **20** (4%) (Table 2), after flash column chromatography.

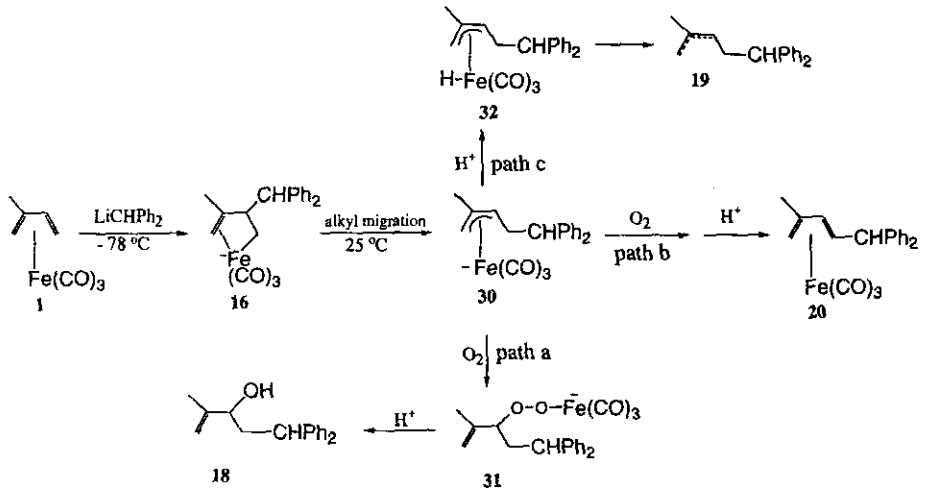
^{1}H NMR and IR spectra of compound **18** provided initial evidence to support the structural assignments. The ^{1}H NMR spectrum of **18** exhibited the following: a multiplet (δ 7.22-7.40 ppm), assigned to protons at phenyl groups; two singlets at δ 4.88 and 4.89 ppm, assigned to vinyl protons; a doublet of doublets, centered at δ 4.13 ppm, assigned to the methine proton (allylic position); a doublet of doublets, centered at δ 3.89 ppm, assigned to the methine proton (benzylic position); a multiplet, centered at δ 2.25 ppm, assigned to methylene protons; a singlet at δ 1.72 ppm, assigned to methyl protons. The IR spectrum of compound **18** exhibited: a broad absorption centered at 3599 cm^{-1}, assigned to the hydroxyl group. A possible mechanism to form compounds **18-20** appears in Scheme IV. Nucleophilic addition (diphenylmethyl anion) presumably occurred initially at the internal position of complex **1** at -78 °C. Upon warming, the nucleophile reversed and added at the terminal position of the diene ligand to generate the more stable tricarbonyl(η^3-allyl)iron(0) anion complex **30**. Oxidation of **30** with dioxygen occurred with insertion to give peroxo inter-

Table 2. Reaction of (η^3-Allyl)Fe(CO)$_3$ Anionic Complexes with Dioxygen

Entry	Complex	Nucleophile (oxidant)	Products (yield/%)[a]
1	 1	$LiCHPh_2$ (O_2/H^+)	 18 (48) 19 (32) 20 (4)
2	 8	$LiCHPh_2$ (O_2/H^+)	 21 (22) 22 (11)[b]
3	 11	$LiCHPh_2$ (O_2/H^+)	 23 (35)
4	11	$LiC(CH_3)_2CN$ (O_2/H^+)	 24 (15) 25 (6)
5	 9	$LiCHPh_2$ (O_2/H^+)	 26 (6) 27 (42) 28 (13)
6	 10	$LiCHPh_2$ (O_2/H^+)	 29 (14)

[a] Satisfactory spectral data (IR, ^{1}H and ^{13}C NMR, high resolution mass spectra) were obtained for all compounds. Yields are based on isolated yields of analytically pure compounds.
[b] The product was further oxidized from **21**.

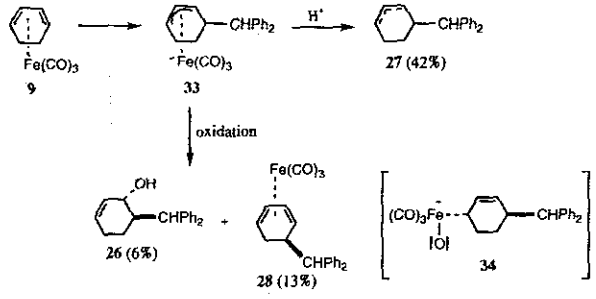
Scheme IV



mediate **31**. Protonation of **31** with trifluoroacetic acid produced **18** (path a). Oxidation of **30** with dioxygen gave nucleophilically substituted iron-diene complex **20** (path b). The reaction pathway is also proposed for bromination and methylation of $(\eta^3$-allyl)$Fe(CO)_3$ anion complexes.[5,6b] An iron hydride species **32** was obtained upon direct quenching of **30** with CF_3CO_2H (path c). Reductive elimination of **32** followed by decomplexation of the iron tricarbonyl moiety gave **19**. The reaction proceeded smoothly for several combinations of addition and oxidation. The results are summarized in Table 2.

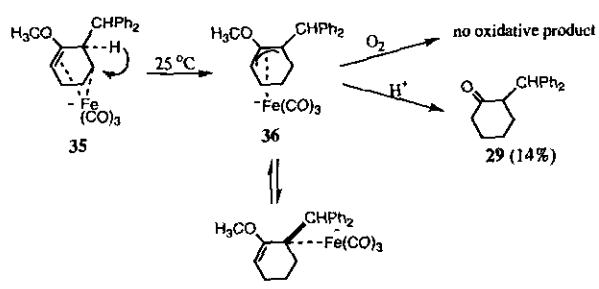
In general, addition of reactive nucleophiles to diene-iron complexes at 25 °C followed by oxidation gave an allylic alcohol as the major product (entries 2-4, Table 2). However, with a cyclic substrate, for example complex **9**, oxidation of **33** failed. The major product isolated was olefin **27** (42%), which derived from acid is quenching of **33**. The oxidation products such as alcohol **26** and complex **28** were isolated as minor products (Scheme V).

Scheme V



The reason for the distinction is unclear. Insertion of dioxygen into the C-Fe bond in cyclic $(\eta^3$-allyl)$Fe(CO)_3$ intermediate **33** might be difficult because of steric hindrance. Thus, protonation of **33** gave **27**. Formation of trans isomer **26** is consistent with addition of the nucleophile from the opposite side of the iron tricarbonyl moiety, followed by insertion of dioxygen into the C-Fe bond.[1c] Compound **28** might be formed from $(\eta^1$-allyl)$Fe(CO)_3$ **34** after β-hydride elimination and recoordination of the $Fe(CO)_3$ moiety to the pendant double bond. In the special case, complex **10** with a methoxy group at the C-2 position of the diene ligand under the general procedure yielded no oxidative product (Scheme VI). Treatment of the carbanion with **10** at -78 °C gave homoallyl anion **35**. Upon warming, anion **35** rearranged to give the more stable species **36**, presumably via β-hydride elimination and readdition.[2b] Reaction of **36** with acid would give **29**. The failure of an oxygen atom to insert into **36** is not understood. An electron-releasing group such as methoxy at the allyl ligand might push the anionic tricarbonyl moiety from the alkene ligand to generate **37**. Thus insertion of an oxygen atom into the tertiary carbon-iron in $(\eta^1$-allyl)$Fe(CO)_3$ would be difficult because of steric hindrance.

Scheme VI



In conclusion, we have shown that oxidation of (η^1,η^2-but-3-en-1-yl)Fe(CO)$_3$ (homoallyl) anion intermediates with dioxygen gives γ,δ-unsaturated acids in good yields. The result is consistent with reaction of (η^1,η^2-but-3-en-1-yl)Fe(CO)$_3$ anion complexes with dibromine. Reaction of acyclic (η^3-allyl)Fe(CO)$_3$ anion intermediates with dioxygen produced allylic alcohols after acid is quenching. Further development of these processes is in progess in our laboratories.

EXPERIMENTAL SECTION

General Information

All tricarbonyliron complexes were synthesized according to known methods.[12,6a,2a] The term "concentration" refers to the removal of solvent with an aspirator pump (Cole-Parmer, Model 704900, with a Buchi Rotovapor-R). The term "under nitrogen" implies that the apparatus was evacuated (oil pump) and then filled with dinitrogen three times. Melting points determined in open capillaries (Yamato MP-21 apparatus) are uncorrected. ^{1}H NMR spectra were obtained with JEOL-EX 400 (400 MHz) spectrometer. The chemical shifts are reported on a scale in ppm with either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as internal standards. ^{13}C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO FT/IR-5300 spectrometer. Mass spectra were measured on a JEOL JMS-D 100 spectrometer at an ionization energy 70 eV and are reported as mass/charge (m/z) with relative abundance. High-resolution mass-spectra (HRMS) data were obtained on an JEOL JMS SX/SX-102A instrument in the Department of Chemistry of National Chung-Hsing University, Central Instrument Center, Taichung. Flash-column chromatography, following the method of Still,[10] was carried out with silica gel (Merck, Kieselgel 60, 230-400 mesh) using the indicated solvents. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F_{254} plastic plates of 0.2-mm thickness (Merck, Germany). Spots on the TLC plate were made visible with UV light or sulfuric acid (1%) and *p*-anisaldehyde (1%) in ethanol. Tetrahydrofuran (THF) and diethyl ether (ether) were distilled under dinitrogen from benzophenone ketyl immediately before use. Hexamethylphosphoramide (HMPA, Aldrich) diisopropylamine (Aldrich), diphenylmethane (Aldrich) and isobutylnitrile (Aldrich) were distilled from calcium hydride (under reduced pressure as necessary) and stored under dinitrogen. Butyllithium was used as a solution in hexane. Diironnonacarbonyl was obtained by photolysis of ironpentacarbonyl in benzene and acetic acid according to the literature procedure.[11]

Generation of 1-Lithio-1,1-diphenylmethane

To a solution of diphenylmethane (0.25 mL, 1.50 mmol) in THF (3 mL), in a Schlenk tube equipped with a rubber septum and a magnetic stirrer, under dinitrogen at -78 °C, was added rapidly via syringe a solution of *n*-butyllithium (1.50 M in hexane, 1.35 mmol, 0.9 mL), followed by addition of hexamethylphosphoramide (HMPA, 1 mL). The resulting orange-red solution was stirred at 0 °C for 1.5 h. This solution was used immediately to react with iron complexes (1 mmol in 1 mL THF, see below).

Generation of 2-Lithio-2-methylpropionitrile

To a solution of diisopropylamine (0.21 mL, 1.50 mmol) in THF (3 mL), in a Schlenk tube equipped with a rubber septum and a magnetic stirrer, under dinitrogen at -78 °C, was added rapidly via syringe a solution of *n*-butyllithium (1.50 M in hexane, 1.35 mmol, 0.9 mL). The reaction mixture was stirred at -78 °C for 20 min. To the solution prepared above was added rapidly via syringe neat 2-methylpropionitrile (0.13 mL, 1.4 mmol), followed by addition of hexamethylphosphoramide (HMPA, 1 mL). The resulting light yellow solution was stirred at -78 °C for 20 min. This solution was used immediately in reaction with iron complexes (1 mmol in 1 mL THF, see below).

General Procedure I: Addition of Anions to (η^4-1,3-dienes)Fe(CO)$_3$ Complexes at -78 °C Followed by Oxidation with Molecules of Dioxygen

To a solution of anion (1.50 mmol, see above) at -78 °C was added rapidly via syringe a solution of (η^4-diene)Fe(CO)$_3$ complex in THF (1 mmol, 1 mL). The reaction mixture was stirred at -78 °C for 2 h. Dioxygen was added via syringe bubble at -78 °C for 1 h. The reaction was quenched with trifluoroacetic acid, and then stirred at 25 °C for 1 h. The resultant reaction mixture was diluted with ethyl acetate (200 mL). The solution was then extracted with water (three 100-mL portions), saturated brine solution (2 × 100 mL), dried over magnesium sulfate, filtered through celite, and finally concentrated on a rotary evaporator.

General Procedure II: Addition of Anions to (η^4-1,3-dienes)Fe(CO)$_3$ Complexes at 25 °C Followed by Oxidation with Dioxygen

To a solution of anion (1.50 mmol, see above) at -78 °C was added rapidly via syringe a solution of (η^4-di-

ene)$Fe(CO)_3$ complex in THF (1 mmol, 1 mL). The reaction mixture was stirred at 25 °C for 2 h. Dioxygen was added via syringe bubble at -78 °C for 1 h. Neat trifluoroacetic acid was added via syringe at -78 °C to the reaction mixture. The reaction was then stirred at 25 °C for 1 h. The resultant reaction mixture was diluted with ethyl acetate (200 mL) and then extracted with water (3 × 100 mL), and saturated brine solution (2 × 100 mL), dried over magnesium sulfate, filtered through celite, and finally concentrated on a rotary evaporator.

Formation of 3-diphenylmethyl-4-methyl-4-pentenoic Acid (12)[6a]

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 3 mmol; complex **1**, 2.4 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (17% ethyl acetate in hexane) to provide acid **12** (0.42 g, 1.47 mmol, 61%).

Formation of (2S*,3S*) (E) 3-diphenylmethyl-2-methyl-4-hexenoic Acid (13)[6a]

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 2.4 mmol; complex **8**, 2 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (17% ethyl acetate in hexane) to provide acid **13** (0.50 g, 1.68 mmol, 84%).

Formation of (1R*,2S*) 2-diphenylmethyl-3-hexenoic acid (14)[6a]

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 1.2 mmol; complex **9**, 1 mmol; under dioxygen trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (33% ethyl acetate in hexane) to provide acid **14** (0.183 g, 0.63 mmol, 63%).

Formation of (1S*,4R*,8R*) 8-diphenylmethyl-3-oxo-4-methoxybicylo[3.2.1]octan-2-one (15)[6a]

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 1.2 mmol; complex **10**, 1 mmol; under dioxygen and trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (17% ethyl acetate in hexane) to provide lactone **15** (0.21 g, 0.65 mmol, 65%).

Formation of 5,5-diphenyl-3-hydroxy-2-methyl-1-pentene (18), 5,5-diphenyl-2-methyl-1-pentene and 5,5-diphenyl-2-methyl-2-pentene (19)[2b] **and Tricarbonyl-[(1,2,3,4-η)-5,5-diphenyl-2-methylpenta-1,3-diene]iron (20)**[6b]

The reaction mixture derived using General Procedure II (1-lithio-1,1-diphenylmethane, 3 mmol; complex **1**, 2.4 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (17% ethyl acetate in hexane) to provide alcohol **18** (0.29 g, 1.15 mmol, 48%), olefin isomers **19** (0.15 g, 0.64 mmol, 32%) and complex **20** (0.02 g, 8 mmol, 4%); alcohol **18** IR (CH_2Cl_2) 3599, 3069, 3030, 2945, 1651, 1599, 1493, 1450, 1375, 1294, 1159, 1053, 1030, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.22 (m, 10 H, Ph), 4.89 (s, 1 H), 4.88 (s, 1 H), 4.13 (dd, J = 8.8, 6.8 Hz, 1 H), 3.89 (dd, J = 8.4, 5.4 Hz, 1 H), 2.25 (m, 2 H), 1.72 (s, 3 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 147.4, 144.8, 144.1, 128.5, 128.4, 128.0, 127.8, 126.3, 126.2, 111.4, 73.7, 47.4, 40.8, 17.4 ppm; MS (70 eV) *m/z* (rel intensity) 252 (M^+, 5), 234 (19), 219 (8), 180 (47), 167 (100), 152 (17), 105 (33), 77 (27); HRMS (EI) calcd for $C_{18}H_{20}O$ (M^+) 252.1514, found *m/z* 252.1518.

Formation of (2S*,5S*) (E) 5-diphenylmethy-2-hydroxy-3-pentene (21) and (E) 5-diphenylmethyl-3-penten-2-one (22)

The reaction mixture derived using General Procedure II (1-lithio-1,1-diphenylmethane, 1.5 mmol; complex **8**, 1 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (17% ethyl acetate in hexane) to provide alcohol **21** (0.058 g, 0.22 mmol, 22%) and ketone **22** (0.29 g, 0.11 mmol, 11%); alcohol **21** IR (CH_2Cl_2) 3599, 3069, 3043, 2982, 2932, 1658, 1494, 1450, 1421, 1377, 1273, 1263, 1078, 1043, 898, 858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.10 (m, 10 H, Ph), 5.43 (dd, J = 15.4, 7.5 Hz, 1 H), 5.34 (dd, J = 15.4, 6.6 Hz, 1 H), 4.06 (m, 1 H), 3.60 (d, J = 10.7 Hz, 1 H), 3.02 (m, 1 H), 1.08 (d, J = 6.3 Hz, 3 H), 0.97 (d, J = 6.8 Hz, 3 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 142.1, 133.6, 132.7, 126.9, 126.6, 126.5, 124.7, 124.5, 67.2, 57.3, 38.9, 21.3, 18.0 ppm; MS (70 eV) *m/z* (rel intensity) 264 ($M^+ - H_2$, 1), 248 (12), 233 (3), 219 (13), 208 (11), 183 (3), 167 (100), 152 (17), 128 (8), 115 (8), 91 (15), 43 (38); HRMS (EI) calcd for $C_{19}H_{20}O$ ($M^+ - H_2$) 264.1514, found *m/z* 264.1518; ketone 22 IR (CH_2Cl_2) 3067, 3030, 2986, 1672, 1626, 1494, 1450, 1361, 1249, 1174, 1091, 979, 902, 883 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.15 (m, 10 H, Ph), 6.62 (dd, J = 16.1, 7.8 Hz, 1 H), 6.00 (d, J = 16.1 Hz, 1 H), 3.72 (d, J = 10.7 Hz, 1 H), 3.24 (m, 1 H), 2.08 (s, 3 H), 1.04 (d, J = 6.8 Hz, 3 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 198.7, 151.9, 143.0, 130.8, 128.7, 128.5, 128.1, 128.0, 126.5, 58.1, 40.8, 26.7, 19.0 ppm; MS (70 eV) *m/z* (relative intensity) 264 (M^+, 2), 248 (6), 219 (6), 167 (100), 152 (42), 115 (14), 105 (14), 91 (20), 43 (38); HRMS (EI) calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found *m/z* 264.1508.

Formation of 2,3-dimethyl-5,5-diphenyl-3-hydroxy-1-pentene (23)

The reaction mixture derived using General Procedure II (1-lithio-1,1-diphenylmethane, 2.4 mmol; complex **11**, 2 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (9% ethyl acetate in hexane) to provide alcohol **23** (0.20 g, 0.69 mmol, 35%); IR (CH_2Cl_2) 3576, 3086, 3030, 2978, 2954, 1599, 1493, 1450, 1375, 1263, 1082, 1001, 866 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.14 (m, 10 H, Ph), 4.97 (s, 1 H), 4.89 (s, 1 H), 4.02 (dd, J = 8.5, 4.8 Hz, 1 H), 2.52 (dd, J = 14.2, 8.5 Hz, 1 H), 3.39 (dd, J = 14.2, 4.8 Hz, 1 H), 1.73 (s, 3 H), 1.24 (s, 3 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 150.0, 145.9, 144.9, 128.8, 128.5, 128.1, 127.5, 126.5, 126.1, 110.5, 76.3, 47.3, 45.3, 28.2, 19.6 ppm; MS (70 eV) *m/z* (rel intensity) 248 (M^+ - H_2O, 78), 233 (35), 181 (100), 167 (57), 99 (8), 86 (67); HRMS (EI) calcd for $C_{19}H_{20}$ (M^+ - H_2O) 248.1565, found *m/z* 248.1564.

Formation of 4-hydroxy-2,2,4,5-tetramethyl-5-hexenenitrile (24) and 2,2,4,5-tetramethyl-4-hexenenitrile (25)

The reaction mixture derived using General Procedure II (2-lithio-2-methylpropionitrile, 3 mmol; complex **11**, 2.7 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated by on a flash-column chromatograph (9% ethyl acetate in hexane) to provide alcohol **24** (0.062 g, 0.37 mmol, 15%) and olefin **25** (0.032 g, 0.21 mmol, 6%); alchol **24** IR (CH_2Cl_2) 3593, 3055, 2991, 2978, 2923, 2235, 1643, 1452, 1375, 1184, 1095, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.17 (s, 1 H), 5.01 (s, 1 H), 1.85 (d, J = 7.8 Hz, 1 H), 1.83 (s, 3 H), 1.81 (d, J = 7.8 Hz, 1 H), 1.42 (s, 9 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 149.9, 125.6, 110.7, 75.2, 48.4, 30.3, 29.8, 28.6, 28.3, 19.9 ppm; MS (70 eV) *m/z* (rel intensity) 167 (M^+, 10), 152 (28), 127 (52), 110 (20), 91 (100), 85 (90), 69 (70), 57 (85); HRMS (EI) calcd for $C_{10}H_{17}NO$ (M^+) 167.1310, found *m/z* 167.1312; olefin 25 mp 115-117 °C; IR (CH_2Cl_2) 3053, 2980, 2934, 2870, 2233, 1460, 1338, 1277, 1182, 895 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 2.10 (s, 2 H), 1.80 (s, 3 H), 1.70 (s, 3 H), 1.36 (s, 6 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 133.7, 125.8, 123.8, 44.3, 33.4, 32.3, 27.3, 27.4, 20.3, 18.8 ppm; MS (70 eV) *m/z* (rel intensity) 151 (M^+, 100), 137 (12), 123 (20), 95 (17), 82 (37), 79 (12), 55 (12); HRMS (EI) calcd for $C_{10}H_{17}N$ (M^+) 151.1360, found *m/z* 151.1359.

Formation of (3R*,4R*) 4-diphenylmethyl-3-hydroxycyclohexene (26), 4-diphenylmethylcyclohexene, 3-diphenylmethylcyclohexene (27)[2a] and Tricarbonyl-[(1,2,3,4-η) exo 5-diphenylmethylcyclohexa-1,3-diene]iron (28)[6b]

The reaction mixture derived using General Procedure II (1-lithio-1,1-diphenylmethane, 2.4 mmol; complex **9**, 2 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (17% ethyl acetate in hexane) to provide alcohol **26** (0.035 g, 0.13 mmol, 6%), olefin isomers **27** (0.21 g, 0.84 mmol, 42%) and complex **28** (0.10 g, 0.26 mmol, 13%); alcohol **26** IR (CH_2Cl_2) 3590, 3067, 3028, 2920, 1599, 1493, 1450, 1273, 1261, 1055, 1008, 896, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.12 (m, 10 H, Ph), 5.93 (dt, J = 9.8, 3.4 Hz, 1 H), 5.67 (dd, J = 9.8, 2 Hz, 1 H), 3.92 (brs, 1 H), 3.83 (d, J = 10.2 Hz, 1 H), 2.61 (m, 1 H), 1.99 (m, 2 H), 1.82 (m, 1 H), 1.35 (m, 1 H) ppm; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 143.9, 130.7, 128.8, 128.5, 128.2, 128.1, 128.0, 126.5, 126.3, 67.8, 53.1, 43.9, 22.9, 21.8 ppm; MS (70 eV) *m/z* (rel intensity) 264 (M^+, 2), 246 (3), 186 (4), 167 (100), 97 (33), 70 (6); HRMS (EI) calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found *m/z* 264.1520.

Formation of 2-diphenylmethylcyclohexanone (29)[2b]

The reaction mixture derived using General Procedure II (1-lithio-1,1-diphenylmethane, 1.5 mmol; complex **10**, 1 mmol; under dioxygen; trifluoroacetic acid, 1 mL) was separated on a flash-column chromatograph (4% ethyl acetate in hexane) to provide ketone **29** (0.038 g, 0.14 mmol, 14%).

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Diene iron complex; γ,δ-Unsaturated acids; Allylic alcohols.

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